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"Aromaticity of NIR absorbing dyes: a Computational study by ab-initio and DFT methods."

Ph.D. Synopsis

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INRODUCTION

Recently in the development of dyes there has been much attention in the area of organic and organometallic dyes. Few area of interest are optical devices, Sensor, Dye sensitized solar cell, photocatalysis, organic light-emitting diodes, etc. like gallium aluminum arsenide and indium phosphide diode lasers are widely used as a light source[1,2]. Since dyes absorbing in the near-infrared (NIR) region (i.e. beyond about 700 nm in wavelengths and less than about 14000 cm^{-1} in wavenumbers) are required and the oscillator wavelengths fall in the near-infrared region, they are suitable applicants[3,4]. Near infrared excitable complexes are particularly useful for sensor, because they have much lower levels of autofluorescence (compared to UV–vis dyes) and lower light scattering, and because of their potential for measurements in tissues and living organisms. Because of the singlet oxygen that is produced upon quenching, some complexes also find application in photodynamic therapy[5]. Literature data on NIR dyes is extremely limited. Recent books on color chemistry contain only sparse information and only a few references have appeared[6-8]. Some dyes have, however, been discussed in other contexts such as quantum electronics and optoelectronic[9-11].

The first NIR absorbing organic compounds were synthesized at the beginning of this century. Comparison of the visual color of oxidation products of phenylenediamines and benzidines led J. Piccard to the conclusion that light absorption of them should occur in the near-IR regions[12]. Various NIR polymethine dyes became accessible at the beginning of the **1930s** and proved very useful in photographic sensitization up to **1300 nm**.

Some natural porphyrines as well as various related synthetic cyclic chromophores proved to be near-IR absorbing dyes. Compounds absorbing at long wavelengths in the visible and near-infrared region are now generally called “deeply colored” dyes. This review includes near-IR chromophores which absorb light due to their π-electronic systems. Both closed- and open-shell structures are discussed. The multitude of spectral data necessarily requires some arbitrary selection. Attempts have been made to select representative examples. In this review attention has also been directed toward the most recent fields of application. Chromophoric systems that are not of practical use because of their low stability or low absorption coefficients are mentioned only in passing.

Density functional theory or DFT is a quantum mechanical method that tries to calculate the electron density directly, without first finding the wave function. In this When compared to HF techniques, DFT has several advantages. Density functional theory treats electron correlation exactly while HF neglects it completely. Although post-HF methods such as MP (Møller-Plesset) and CC (coupled-cluster) can be used to take into account electron correlation, DFT gives results of comparable or better quality at a computational cost similar to HF.

In terms of computational efficiency, in principle DFT scales as N^3, where N is the number of basis functions used to represent the KS orbitals. This compares with N^4 for HF. Slater-type orbitals (STOs) may be used instead of contracted Gaussiantype orbitals (GTOs), thus reducing the number of orbitals necessary. The original motivation to use GTOs was to allow analytical integration of four-centre two way it differs from the semi-empirical and *ab initio* methods described earlier. In DFT the problem of finding the wave function of a system is replaced by the similar problem of finding the electron density. electron integrals, but this is not necessary in DFT calculations.

Furthermore, convergence with respect to basis-set size tends to be more rapid than for HF techniques. DFT has the ability to provide formal expressions for quantities of chemical interest, most of which are not easily defined in HF theory. These include electronegativity, global hardness and softness, local hardness and softness, and the Fukui function. These can be used to rationalise trends in reactivity, site specificity, etc. One of the problems with DFT is that it is necessary to use approximate functional to calculate Exc. In addition, it is not clear how to improve a functional. There is no progression in levels of theory which allows the calculation of molecular properties with increasing accuracy, thus allowing extrapolation to the exact answer, as is possible with HF and post-HF methods. Weak interactions such as van der Waalstype interactions are poorly described by current functionals, although hydrogen bonding is reasonably well accounted for.

The Kohn-Sham (KS) orbitals that arise in DFT calculations represent the molecular orbitals of a fictitious system of non-interacting electrons. It is not universally accepted that it is valid to discuss the KS orbitals as physically meaningful orbitals, although the KS orbitals have been shown to be very similar to the molecular orbitals calculated from HF theory.14 In addition, it has been proven that for the exact density functionals the eigenvalue of the highest occupied

orbitals is equal to the first ionisation potential.15 It should also be noted that DFT tends to favour delocalised structures over localised ones.

Before the advent of DFT, the semi-empirical modified-INDO method of Zerner (ZINDO) was the primary tool used to study the electronic structure and spectra of transition metal systems. Parameters for Ru complexes were available since 1990. Daul, Baerends and Vernooijs**.** were the first to use density functional theory to investigate the electronic properties of a ruthenium polypyridyl-type complex. Baerends is one of the authors of the Amsterdam Density Functional (ADF) program package, which they used in this study. Using a crystal structure of D3 symmetry, they predicted from first principles the energetic ordering of the components of them MLCT excited state manifold of [Ru(bpy)3]2+. The calculated transition energies showed an acceptable agreement with experiment, though not enough to unambiguously describe the fine structure of the MLCT manifold of [Ru(bpy)3]2+.

[Ru(bpy)3]2+ was also the first ruthenium polypyridyl complex to be geometryoptimised using DFT. Buchs and Daul used the ADF package with the Vosko, Wilk and Nusair (VWN) functional in the local density approximation (LDA). A comparison with the crystal structure of the geometries obtained using a GGA functional and the LDA functional showed the LDA to perform better. The largest difference was found for the Ru-N bond length: 2.056Å (X-ray), 2.050Å (LDA), 2.099Å (GGA). This tendency of the GGA to overestimate the metal-ligand distance had previously been found for other Werner complexes. The calculation correctly predicted a slight dihedral angle between the two rings of each bipyridine unit. The energy of the 3MC was calculated, assuming the same geometry as the ground state. The result was 1.5 times the experimental value. The authors concluded that due to the long lifetime of the 3MLCT, vibrational relaxation had time to occur before the 3MC was populated. They noted that the energy of the MC transition was lowered when the calculation was repeated with increasing Ru-N bond lengths, as expected.

REVIEW OF LITERATURE AND DEVELOPMENT IN THE SUBJECT

- **Review of R&D in the proposed area (National & International Status, Importance, patents etc.)**

International status:

Numerous functional have been proposed for DFT calculations. The well-known and broadly used Becke3–Lee–Yang–Parr hybrid functional (B3LYP) was favored in this study over the parameter free Perdew–Burke–Enzerh of hybrid functional (abbreviated as PB0 or PBE1PBE). The PB0-functional was recommended by Jaquemin et al. in studies of classical dyes. In critical cases, however, both functionals were used in this study. The most frequently employed Pople-type Gaussian-type basis sets in DFT calculation is the valence double-x basis set 6-31 þ G*. Smaller basis sets are generally less suited. To achieve convergence in the calculated p/p* transition energies more extended basis sets were used by Jacquemin et al. The standard basis set 6-31 þG* was generally employed in the calculation of the optimum geometry and the spectral excitation and more extended basis sets only if the results were unsatisfactory. Since the aim of this study was not to accurately reproduce numerical values but rather to screen a large number of different chromophoric compounds the simplified theoretical model appears adequate. Solvent effects were disregarded although the calculation may improve the transition energy of dyes calculated at too short wavelengths. However, the solvents used in the spectroscopic studies of the selected dyes vary greatly. As far as possible, spectral data were selected in less polar solvents. According to former studies the mean absolute error (MAE) of the calculated TDDFT excitation energies without consideration of the solvent effect amounts to about 0.21 eV .

National status

Numerous functionals have been proposed for DFT calculations. Ch. Prabhakar , K.Yesudas, G.Krishna Chaitanya,Sanyasi sitha,k.bhanuprakash and V. jayathirtha rao carried out high-level symmetry-adapted cluster-configuration interaction (SAC−CI) calculations of some substituted SQ and CR dyes and compare the absorption energy with the existing experimental data The diradical character of the ground state singlets of several oxyallyl derivatives arecarried out by Kola shriniwas and their team as the oxyallyl derivatives like squaraine and croconate dyes can be represented by both mesoionic and diradical formulas, the domination of which would

characterize its lowest energy transition. Apart from that, there are no much studies on aromaticity of NIR absorption dyes upto my knowledge at national level.

- ***Objectives of the proposed project***

Keeping in the view of above mentioned points and the recent theoretical calculations the following objectives have been framed out, more particularly based on some of the NIR absorbing organic and organometallic dyes.

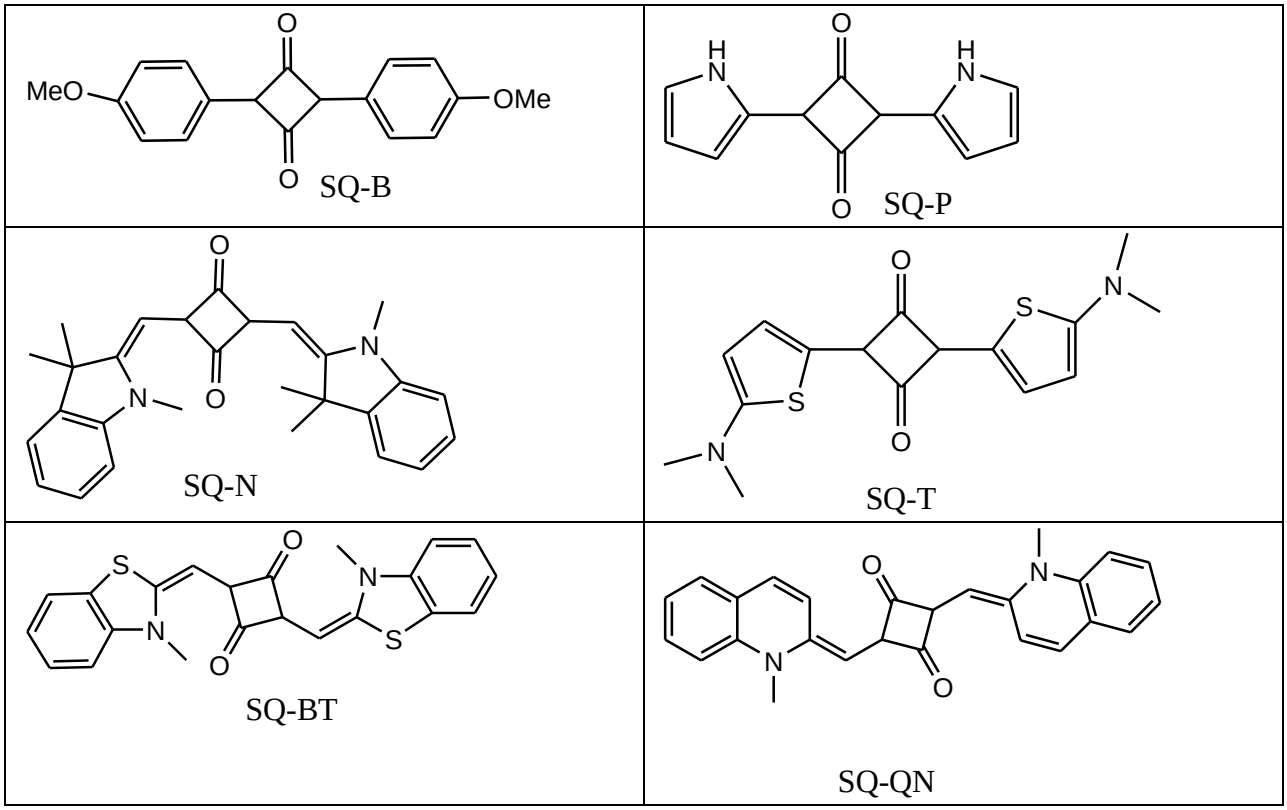
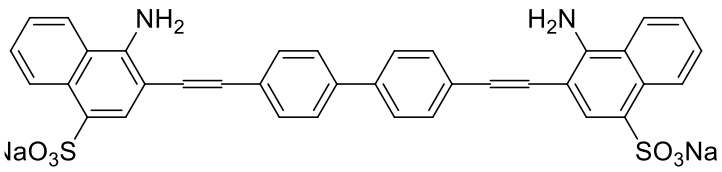
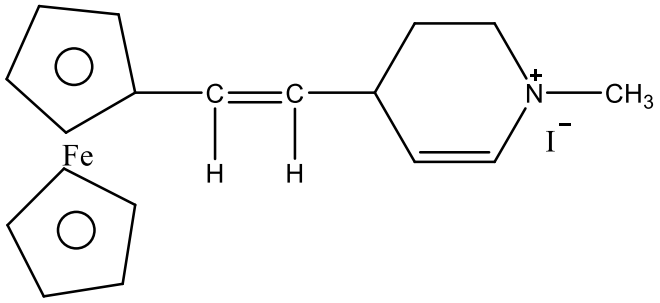


Figure 1: proposed structures of Near IR Dyes



Congo Red dye



Ferrocine derived organometallic dyes

- Study of ground state electronic structure of organic and organometallic NIR absorbing dyes.
- Calculation of aromaticity by various methods like HOMED,NICS,MCI methods etc
- Proposing new new dye derivatives for experimental chemists.

- **Work plan (including *detailed methodology* and time schedule)**

Methodology

Ground state geometry optimization of the Near infrared absorbing dyes will be carried out for the both singlet and triplet states using *ab initio* and density functional theory (DFT) methods. To locate the actual minima on the potential energy surface of these molecules the vibrational frequency calculations also will be done to ensure that there are no imaginary frequencies. The conventional coupled cluster (CC) methods have been considered as cheaper methods than configurational interaction (CI) methods. But the limitation enters here as the excitation energies will be highly deviated from the experimental values when the contribution of double excitation rises to dominate. Even CC methods are failed in the case where internal conversion between ground state and excited state occurs. In this regard newly developed time dependent DFT (TD-DFT) methodology, which has been considered as a standard tool to obtain the

ground and excited state electronic structures will be used. The calculations can be carried out by using HOMED,PDI and NICS methods to give effective results.

It is improper if we do not include the solvent effects in these calculations, since the experimental absorption or emission spectra usually are obtained in solvent media. Hence to study the effect of solvent polarity on the ground state or excited state geometries this study includes polar continuum model (PCM) or Onsager models to simulate the bulk solvent effects.

PROPOSED WORK PLAN/FORMULATION AND STRUCTURE OF STUDY

Year	Activities
I – Year	Literature survey and initial training
	ground state PES calculation of Near infrared absorbing Dyes
II – Year	Calculation of aromaticity by HOMED and NICS
III – Year	Calculation of aromaticity by MCI and PDI method
	Compilation of the data for publications and preparing the final report

References:-

1) Jones,F. Reu.Prog. *Color.Relut. Top.* 1989,19,20.
2) Matauoka, M. *J. SOC. Dyers Colour.* 1989,105, 167.
3) Griffiths, J. *J. SOC. Dyers Colour.* 1988, 104, 416.
4) Yoshida, Z., Kitao, T., Eds. *Chemistry of Functional Dyes;* Mita Prese: Tokyo, 1989.

5) Zollinger, M. Colour *Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments;* VCH Weinheim,

6) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants. Theoretical Treatment and Empirical Rules;* Springer
Verlag: Berlin, 1980.

7) Griffiths, J. Colour *and Constitution of Organic Molecules;* Acad. Press: London, 1976.

8) HOnig, S.; Quast, H. In *Optische Anregung organischer Systeme;* Verlag Chemie: Weinheim, 1966 pp 184 ff.

9) Matsuoka, M., Ed. *Infrared Absorbing Dyes;* Plenum: New York, 1990.

10) Artamonova, T. V.; Zakhs, E. R.; Khromenkov, 0. V.; Shaburov, V. V. *Izu. Vys. Ucheb. Zaued., Khim. Techn.* 1989, 32, 2.

11) Matsuoka, M., Ed. *Infrared Absorbing Dyes;* Plenum: New York, 1990. Artamonova, T. V.; Zakhs, E. R.; Khromenkov, 0. V.; Shaburov, V. V. *Izu. Vys. Ucheb. Zaued., Khim. Techn.* 1989,32, 2.

12) Piccard, J. *Ber. Dtsch. Chem. Ges.* 1913, 46, 1843; *J. Am. Chem. Soc.* 1926, 48, 2352.

13) Kdnig, W. *2. Wiss. Photogr. Photophys. Photochem.* 1935, 34, 15.

14) Dieterle, W.; Zeh, W. *Wiss.Photogr.Photophys.Photochem.* 1935, 34, 245.

15) W. Kaim, *Coord. Chem. Rev.*, 2002, **230**, 127;

16) W. Kaim, A. Klein and M. Gl¨ ockle, *Acc. Chem. Res.*, 2000, **33**, 755;

17) J. M. de Wolf, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *New J. Chem.*, 1991, **15**, 501;

18) H. E. B. Lempers, J. G. Haasnoot, J. Reedijk, R. Hage, F.Weldon and J. G. Vos, *Inorg. Chim. Acta.*, 1994, **225**, 67;

19) B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334.

20) D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Aust. J. Chem.*, 1964, **17**, 325.

21) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

22) D.. S. Jones,A.F.Brown,A.D.Woolfson, A.C. Dennis, L. J.Matchett and S. E. J. Bell, *J. Pharm. Sci.*, 2000, **89**, 563–571.

23) B. Ananda Rao et al. / Sensors and Actuators B *188 (2013) 847– 856*

24) Kola Srinivas,ch.Prabhakar,C.Lavanya Devi,K.Yesudas,K.Bhanuprakash and V.Jayanthirtha Rao J. Phys. Chem. A, *2007, 111 (17), pp 3378–3386*

25) Yaseen, M. A.; Srinivasan, V. J.; Sakadzic, S.; Wu, W.;Ruvinskaya, S.; Vinogradov, S. A.; Boas, D. A. Opt. Express.2009, 17, 22341-22350

26) Zhao, J.; Ji, S.; Guo, H. RSC Adv. 2011, 1, 937-950